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Preparation and characterization of ZnO/PVB anticorrosive coating in marine environment

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Preparation and characterization of ZnO/PVB anticorrosive coating in marine environment

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Abstract. A new composite coating system for corrosion resistance of aluminum alloy was fabricated by spinning-coating method. ZnO was added to the PVB coating system as filler, and a small amount of coupling agent was also added to increase the cross-linking of the coating. The fundamental properties of the coating were characterized by SEM and Adhesion test. Moreover, the corrosion resistance of the coating in 3.5 wt. % NaCl solution was estimated by EIS and potentiodynamic polarization. The results showed that the coating was evenly distributed on the surface of the sample and has good adhesion to the substrate. Electrochemical test results show that the coating has a good protective effect on the aluminum alloy matrix.

1. Introduction

The application of metals in marine environment is more and more extensive, and the safety and economic losses caused by metal corrosion are not to be underestimated [1]. Therefore, effective protection against metals is the key to alleviating this phenomenon. Aluminum alloys are used widely in various fields due to their low density, high strength and easy processing. The surface of the aluminum alloy can spontaneously form a protective film to protect itself, but the aluminum alloy in the marine environment is easily corroded by chloride ions in seawater [2]. Therefore, the protection of the aluminum alloy matrix plays an important role in expanding its application and extending its working time.

More and more methods have been used to improve the corrosion resistance of aluminum alloys, such as catholic protection, addition of corrosion inhibitors, metal surface treatments, etc. [3]. Among them, organic coatings are widely used due to the simple preparation method, low cost and wide application range [4].

Polyvinyl butyral (PVB) is gradually used in the coating field due to its excellent film forming properties, high stretchability, impact resistance, and the presence of hydroxyl groups provides more possibilities for chemical modification [5]. Previous studies have been conducted to add chitosan [6], graphene [7], pyridine derivatives [8], polypyrrole [9], narrow diameter polyaniline [10] and polypyrrole-carbon black [11] as fillers to PVB to prepare composite coatings for metals protection.

ZnO as an additive has been used in plastics, paints, adhesives and other fields, but there are few reports on the use of anti-corrosion coatings [12].

In this paper, the coating was prepared by spinning-coating method and high temperature cross-linking curing method. The effect of ZnO filler on the corrosion resistance of PVB coating was studied.

The basic properties of the coating were characterized and the corrosion resistance of the coating was tested by electrochemical method.

2. Experiment

2.1. Materials
Polyvinyl butyral (M.W.40000-70000) and ZnO (99.8% metals basis, 50±10 nm) were all bought from Shanghai Macklin Biochemical Co., Ltd. Silane coupling agent KH-560 was got from Sinopharm Chemical Regent Co.,Ltd. Poly(methyhydrosiloxane) (viscosity: 15-40mPa.s (20℃)) was bought from Aladdin Industrial Corporation. All chemicals were used as received without further purification.

2.2. Preparation of ZnO/PVB coating
The aluminum alloy samples used in the experiment were sanded to smooth surfaces. After rinsed with acetone, ethanol and deionized water successively, the surface of samples were slightly etched with sodium hydroxide solution. Subsequently, the coating was applied uniformly to the surface of the aluminum alloy samples by spinning- coating process. After all this was done, the samples were dried in vacuum dryer with 100 ℃ for 6 hours. The experimentally prepared coating is very thin with a coating thickness of approximately 100 μm.

2.3. Analysis and characterization
The corrosion properties of samples were characterized by electrochemical analyser (CHI604E) in 3.5 wt. % NaCl solution at room temperature. Three-electrode system was used in which a platinum electrode is a counter electrode, an Ag/AgCl electrode is a reference electrode, and a coated aluminum alloy sheet is a working electrode. The samples were all immersed in 3.5 wt. % NaCl solution for 30min in advance before test. Scanning electron microscope (SEM) measurements were conducted on a Hitachi S-4800 instrument operated at 2KV for gold-sputtered samples. And the adhesion of the coating to the substrate was tested by cross-cut test.

3. Results and discussions

3.1. Corrosion resistance of the composite coating
Electrochemical impedance spectroscopy is an important method to characterize the corrosion resistance of coatings. The greater the impedance, the stronger the corrosion resistance of the coating. The Bode plots of PVB coatings with different content of ZnO is shown in Figure 1(a) and Figure 1(b). From Figure 1(a), with the increase of ZnO, the low-frequency impedance modulus of the coating gradually increases, and the impedance modulus is the largest when the ZnO is 15%, almost reaching 10^7. In combination with Figure 1(b), the peak value of the phase angle in the high frequency region reaches about 80 degrees, and a wide peak is maintained when the ZnO content is 15%.

Figure 1(c) shows the nyquist plot of coatings. The larger the radius of the capacitive resistance arc, the better the corrosion resistance of the coating. It is obviously that the best anticorrosive effect is obtained when the content of ZnO is 15%. On the other hand, the anti-corrosion process of the coating can be roughly simulated by the equivalent circuit, and the implications of the main electrical components are marked in the Figure 1(d), too.

The tafel polarization curve is an important indicator to describe the corrosion resistance of the coating. The higher the potential and the lower the corrosion current density, indicating the better the corrosion resistance of the coating [13]. As can be seen from Figure 2, the potential of the coated sample is significantly positively shifted, and the corrosion current density has decreased by two orders of magnitude compared with the bare aluminum alloy.

Table 1 shows the important feature data in tafel curve. The protective effect of the coating on the metal substrate is expressed by the protection efficiency and is calculated by the following formula. The results are also shown in Table 1.

$$\eta = \frac{I^{0}_{corr} - I^{1}_{corr}}{I^{0}_{corr}} \times 100\%$$

Where I^{0}_{corr} and I^{1}_{corr} were the Icorr of bare aluminum and the coating samples with different content of ZnO, respectively [14].

From Table 1, the coating has the lowest corrosion current density and the highest protection efficiency (99%) when the content of ZnO is 10% and 15%. After comprehensively considering the results of electrochemical tests, it was found that ZnO/PVB coating has the excellent protection for aluminum alloys in seawater environments and the best anti-corrosion effect is obtained when the content of ZnO is 15%.

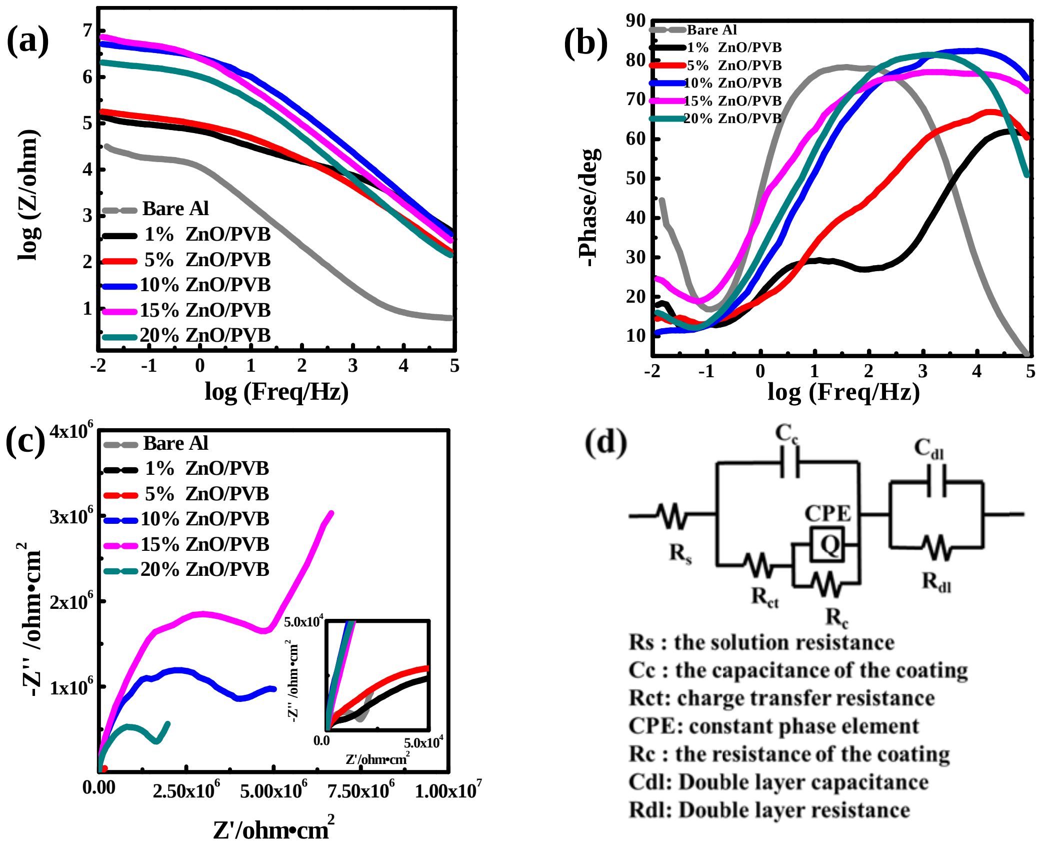

Figure 1. EIS plots of PVB coatings with different content of ZnO in 3.5 wt. % NaCl solution.

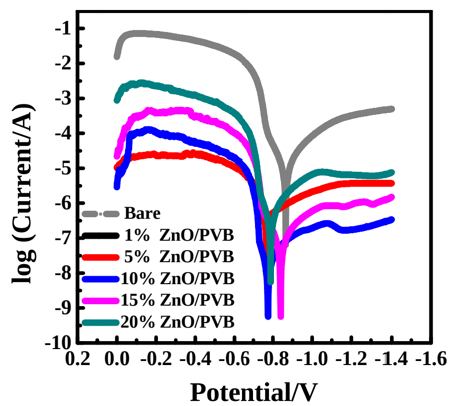

Figure 2. Tafel polarization curves of PVB coatings with different content of ZnO in 3.5 wt. % NaCl solution.

Table 1. Polarization parameters for PVB coatings with different content of ZnO.

Sample	E_{corr} (V)	I_{corr} ($A{\cdot}cm^{-2}$)	R_p	η
Bare	-0.86	8.5×10^{-6}	2.0×10^{3}	
1%ZnO	-0.64	8.6×10^{-7}	4.7×10^{4}	90%
5%ZnO	-0.77	1.3×10^{-6}	3.5×10^{4}	85%
10%ZnO	-0.77	2.2×10^{-8}	9.0×10^{5}	99%
15%ZnO	-0.84	5.0×10^{-8}	2.8×10^{5}	99%
20%ZnO	-0.79	3.1×10^{-7}	4.5×10^{4}	96%

3.2. Microstructure of the composite coating

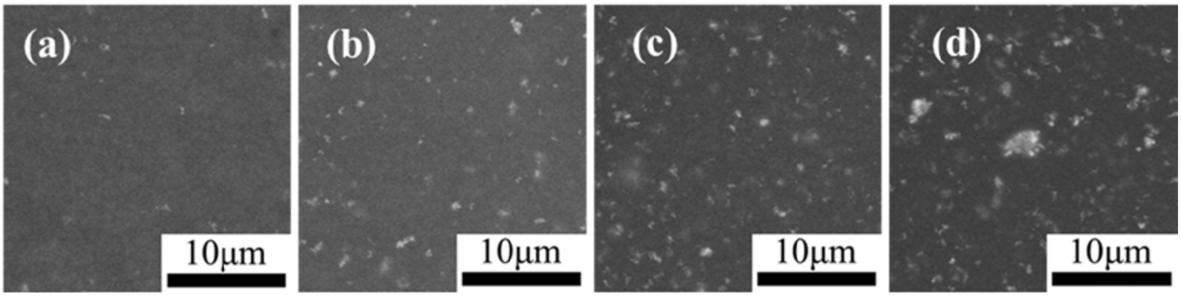

Figure 3. SEM images of ZnO/PVB coatings with (a) 5%, (b) 10%, (c) 15%, (d) 20% ZnO.

Figure 3 shows the surface micromorphology of coating samples with different content of ZnO. As can be seen from it, ZnO is more evenly dispersed on the surface of the aluminum alloy. With the increase of ZnO, the increase of the amount of particles can be observed very clearly, but when the content reaches 20%, the particle size of ZnO increases noticeably. It indicates that excessive ZnO particles deteriorate their dispersibility on the surface of the coating and lead to the occurrence of agglomeration, which is not conducive to the uniformity of the coating, thereby reducing the anticorrosive effect of the coating. All of above prove that the content of the filler is not as good as possible. The uniformity of the coating is the best when the content of ZnO is 15%, which is of great significance for the coating to fully protect the metal matrix.

3.3. Adhesion test of the composite coating

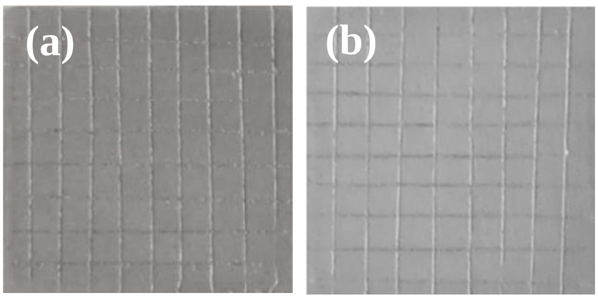

Figure 4. The pictures of ZnO/PVB coatings (a) before and (b) after the coating adhesion test.

The adhesion of coating was characterized by cross-cut test according to the standard of ISO 2409:2012 [15], the results was shown in Figure 4. It is obviously that there is no peeling of the coating in the grid after test, the surface of coating is still intact and look like the same as before, which indicates that the coating has good adhesion, tight and solid bonding with the metal matrix, formed a complete protective layer and therefore has a good protective effect on the metal matrix. The good adhesion of the coating can provide a strong protective layer for the metal matrix and supply guarantees for coating to develop a long-term protective role.

4. Conclusions

A novel PVB coating was successfully prepared for the corrosion protection of aluminum alloy substrates in the marine environment. The results show that the coating has good adhesion, tight and solid bonding with the metal matrix and the ZnO filler is more evenly dispersed on the surface of the aluminum alloy when the content of ZnO is 15%. In addition, the results of electrochemical tests also prove that the ZnO/PVB coating has a significant anti-corrosion effect for aluminum alloy in 3.5 wt. % NaCl solution. Furthermore, the low frequency impedance modulus was about three orders of magnitude higher than bare aluminum, almost reached 10^7 **Ω**•cm^2 and the I_{corr} dropped by almost three orders of magnitude, reached 5.0×10^{-8} A•cm^{-2} when the content of ZnO is 15%. Through comprehensive analysis, we can summarize that the optimum content of ZnO in PVB is 15%.

Acknowledgements

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